

PROCESS TO PREPARE A HEAVY AND A LIGHT LUBRICATING BASE  
OIL

The invention is directed to a process to prepare a heavy and a light lubricating base oil.

Solvent refined processes are well known to prepare base oils having the properties of residual base oils to  
5 light base oils from a petroleum derived source. Light base oils are prepared by solvent refining a lower boiling vacuum distillate stream and the residual base oils are prepared by solvent refining a de-asphalted vacuum residue. Various intermediate grades can be  
10 prepared from the intermediate boiling feedstocks. The resulting base oils could have a kinematic viscosity at 100 °C from 2 cSt for the light base oils to above 30 cSt for the heaviest grades.

There is a tendency in the base oil field to prepare  
15 base oils which contain more saturated components, less sulphur and which have a higher viscosity index than the base oils which can be made by means of the above described solvent refining route. A very suited process is to catalytically dewax the residual fraction obtained  
20 in a fuels hydrocracker process. With a fuels hydrocracker process is meant a process wherein a feedstock is hydroprocessed to mainly middle distillate fuels products. The higher boiling fraction is usually recycled to the hydrocracking step. This bottoms  
25 fraction, also referred to as hydrocracker bottoms, can also be used to prepare base oils. Such a process is for example described in WO-A-9718278 and in WO-A-0250213.

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A disadvantage of the process as described above is that it has been found difficult to prepare the high viscosity product at all or in a sufficient quantity.

The object of the present invention is to provide a process, which can prepare at least a light and a heavy base oil.

The following process achieves this object. Process to prepare a heavy base oil having a kinematic viscosity at 100 °C of above 15 cSt and a light lubricating base oil having a kinematic viscosity at 100 °C of between 3.8 and 6 cSt from a partly isomerised Fischer-Tropsch derived feedstock, said feedstock having an initial boiling point of below 400 °C and a final boiling point of above 600 °C and the fraction boiling above 540 °C is at least 20 wt% by

(a) separating, by means of distillation, said fraction into a light base oil precursor fraction and a heavy base oil precursor fraction,

(b) reducing the pour point of each separate base oil precursor fraction by means of dewaxing,

(c) and isolating the desired base oil products from said dewaxed oil fractions as obtained in step (b).

Applicants have found that with the process according to the invention highly saturated base oils containing almost no sulphur and having a high viscosity index can be prepared. Furthermore different base oil grades may be prepared using this process, ranging from the low viscosity grades to the high viscosity grades. For example a base oil product slate, wherein the different products have kinematic viscosities at 100 °C of about 2, 5, 8.5 and 20 cSt respectively may be prepared in a high yield. A further advantage of dewaxing the light and heavy base oil precursor fractions separately is that the

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pour points of the resulting light and heavy base oils  
can be targeted to their most optimal

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value. If no separate dewaxing is used the pour point of one grade will then be the resultant of the pour point of the other grade. Undesirable quality give away and non-optimal yields per grade will then be unavoidable.

5 Different publications disclose the preparation of Fischer-Tropsch derived base oils. However no publication has disclosed a process for the simultaneous preparation of both low and high viscosity base oils. For example EP-A-1029029, WO-A-0014187 and EP-A-776959 describe the  
10 preparation of low viscosity grade base oil from a Fischer-Tropsch derived feed. The kinematic viscosity at 100 °C of the disclosed base oils ranged from 5.1 to 7.9 cSt. WO-A-0015736 discloses a process in which base oil is obtained from a Fischer-Tropsch derived feed  
15 having a kinematic viscosity at 100 °C of 24.89 cSt.

The preferred feed to step (a) may be suitably the heavy fraction as obtained when hydrocracking a Fischer-Tropsch synthesis product. Such a Fischer-Tropsch synthesis product will comprise mainly normal paraffins  
20 with up to and above 60 carbon atoms. This synthesis product is suitably hydroprocessed (hydroisomerisation/hydrocracking) to convert to one or more middle distillate products and a heavy, atmospheric bottoms product fraction. This heavy bottoms product  
25 fraction having an initial boiling point of below 400 °C and preferably above 300 °C and more preferably above 340 °C will comprise mainly partly isomerised paraffins. An example of a suitable hydroprocessing process for a Fischer-Tropsch synthesis product is  
30 described in EP-A-668342.

The fraction boiling above 540 °C in the feed to step (a) is preferably at least 20 wt% and more preferably at least 30 wt% and most preferably at least

40 wt%. Typically this fraction will be less than 80 wt%. Such heavy Fischer-Tropsch derived feeds may be preferably obtained when a relatively heavy Fischer-Tropsch synthesis product is hydrocracked. Not all  
5 Fischer-Tropsch synthesis processes yield such a heavy product. A preferred Fischer-Tropsch process on which product the feed for the present invention can be based is described in WO-A-9934917 and in AU-A-698392.

In step (a) the feed is separated by means of  
10 distillation into a light base oil precursor fraction and a heavy base oil precursor fraction. The distillation is suitably performed at low (vacuum) pressures, more preferably the vacuum distillation is performed at a pressure of between 0.01 and 0.1 bara. Preferably the  
15 effective cut temperature in step (a) at which the light and heavy base oil precursor fractions are separated is between 470 and 600 °C and more preferably between 480 and 580 °C. The effective cut temperature is the temperature above which 90 wt% of the hydrocarbons  
20 recovered have its boiling point. Suitably the feed is separated into two base oil precursor fractions. Separation into more base oil precursor fractions is also possible. A lower boiling fraction, boiling in the vacuum gas oil range, may also be obtained in the distillation  
25 of step (a) and may be used as gas oil (blending) component or technical white oil.

Step (b) may be performed by means of solvent dewaxing or catalytic dewaxing. Solvent dewaxing is well known to those skilled in the art and involves admixture  
30 of one or more solvents and/or wax precipitating agents with the base oil precursor fraction and cooling the mixture to a temperature in the range of from -10 °C to -40 °C, preferably in the range of

from -20 °C to -35 °C, to separate the wax from the oil. The oil containing the wax is usually filtered through a filter cloth which can be made of textile fibres, such as cotton; porous metal cloth; or cloth made of synthetic materials. Examples of solvents which may be employed in the solvent dewaxing process are C<sub>3</sub>-C<sub>6</sub> ketones (e.g. methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C<sub>6</sub>-C<sub>10</sub> aromatic hydrocarbons (e.g. toluene), mixtures of ketones and aromatics (e.g. methyl ethyl ketone and toluene), autorefrigerative solvents such as liquefied, normally gaseous C<sub>2</sub>-C<sub>4</sub> hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof. Mixtures of methyl ethyl ketone and toluene or methyl ethyl ketone and methyl isobutyl ketone are generally preferred. Examples of these and other suitable solvent dewaxing processes are described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc., New York, 1994, Chapter 7.

Preferably step (b) is performed by means of a catalytic dewaxing process. The catalytic dewaxing process may be any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite,

ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminaphosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in  
5 US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of  
10 possible combinations are Pt/ZSM-35, Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-4343692, US-A-5053373, US-A-5252527 and  
15 US-A-4574043.

The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for  
20 example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania  
25 as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a low acidity refractory oxide binder material, which is essentially free of alumina, is used. Examples of these  
30 binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein  
5 the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite  
10 with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-0029511. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and  
15 dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as for example described in WO-A-0029511 and EP-B-832171.

More preferably the molecular sieve is a MTW, MTT or TON type molecular sieve, of which examples are described  
20 above, the Group VIII metal is platinum or palladium and the binder is silica.

Preferably the catalytic dewaxing of the heavy base oil precursor fraction is performed in the presence of a catalyst as described above wherein the zeolite has at  
25 least one channel with pores formed by 12-member rings containing 12 oxygen atoms. Preferred zeolites having 12-member rings are of the MOR type, MTW type, FAU type, or of the BEA type (according to the framework type code). Preferably a MTW type, for example ZSM-12,  
30 zeolite is used. A preferred MTW type zeolite containing catalyst also comprises as a platinum or palladium metal as Group VIII metal and a silica binder. More preferably the catalyst is a silica bound AHS treated Pt/ZSM-12



containing catalyst as described above. These 12-member ring type zeolite based catalysts are preferred because they have been found to be suitable to convert waxy paraffinic compounds to less waxy iso-paraffinic compounds.

More preferably the above described catalyst comprising the 12-member ring zeolite is used in a first hydroconversion step to lower the pour point of the base oil precursor to a intermediate value between the pour point of the feed and the pour point of the final base oil. More preferably the pour point of the intermediate product is between -10 to +10 °C. The process conditions of such a first step may be suitably the catalytic dewaxing conditions as described below. This first hydroconversion step is followed by a final dewaxing step wherein preferably a catalyst is used which comprises a zeolite having at least one channel with pores formed by 10-member rings containing 10 oxygen atoms. Suitably as 10-member ring zeolites one of the following list comprising a TON type, MFI type, MTT type or FER type is used. The specific catalyst may be one as disclosed above which are according to these zeolite types. A preferred 10-member ring zeolite containing catalyst will also comprise a platinum or palladium metal as Group VIII metal and a silica binder. More preferably the catalyst is a silica bound AHS treated Pt/ZSM-5 or a silica bound AHS treated Pt/ZSM-23 containing catalyst as described above.

In an even more preferred embodiment also the light base oil precursor fraction is catalytic dewaxed as described above for the heavy base oil precursor fraction.

Applicants have found that the two-step process as described above for reducing the pour point may also be used in processes to prepare base oils having a pour point of suitably below -15 °C, more preferably below -20 °C, from a feedstock comprising between 30 and 100 wt% wax, preferably between 50 and 100 wt% wax. The wax content is defined as the wax content which is recovered by solvent dewaxing at -27 °C in a standard methyl-ethylketone toluene mixture.

Such a feedstock may be obtained in a Fischer-Tropsch process such as for example described above. Other suitable feedstocks are the residual fraction obtained in a fuels hydrocracker process or a (hydrotreated) slack wax.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil.

By varying the temperature between 275, suitably between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably +10 °C for the heavier grades to as far down to -60 °C for the lighter grades.

In step (c) the effluents of the separate dewaxing steps are separated by means of distillation into at least a light and heavy base oil grade. The distillation

is suitably performed at low (vacuum) pressures, more preferably the vacuum distillation is performed at a pressure of between 0.01 and 0.1 bará. Preferably the effective cut temperature in step (c) at which the light and heavy base oil fractions are separated is between 470 and 600 °C and more preferably between 480 and 540 °C. Step (c) is preferably performed in one distillation column. Line-ups wherein two or more vacuum distillations columns are used could also be envisaged.

It has been found that with the process of the present invention base oil products may be obtained having a kinematic viscosity at 100 °C of above 15 cSt and more preferably above 17 cSt and most preferably above 20 cSt. Preferably the kinematic viscosity of said products is less than 40 cSt. The pour point of these base oil grades may be below +10 °C, preferably below -10 °C and even more preferably below -20 °C. The viscosity index of these grades are preferably between 140 and 200.

Applicants have found that when these heavy base oil products are used in lubricant formulations less or even no viscosity modifier additive is required. It has been found that especially SAE "xW-y" viscosity lubricant formulations, wherein y-x is greater or equal than 25 may be obtained without having to use a Viscosity Modifier. The SAE J300 classification is meant here the standard as in force at the time of filing of this application. SAE stands for Society of Automotive Engineers in the USA. The "x" number in such a designation is associated with a maximum viscosity requirement at low temperature for that composition as measured typically by a cold cranking simulator (VdCCS) under high shear. The second number "y" is associated with a kinematic viscosity requirement at

100 °C. The heavy base oil may be combined with another Fischer-Tropsch derived base oil to formulate the above lubricant formulations or in combination with other base oils. Other base oils are for example mineral oils,  
5 polyalphaolefins, esters, polyalkylenes, alkylated aromatics, hydrocrackates and solvent-refined basestocks. The invention is also directed to the use of the heavy grade base oil in motor oil formulations which do not require a viscosity modifier.

10 Applicants further found that when a viscosity modifier-free lubricant is used as motor engine lubricant in gasoline direct injection (GDI) engines no build up of residue on the back of the inlet valve tulip occurs.

The invention shall be illustrated by making use of  
15 Figure 1 and 2. Figure 1 shows an example of a preferred embodiment of the process according to the present invention. Figure 2 shows the process of Figure 1 except that two product vacuum distillation columns are used.

In Figure 1 a Fischer-Tropsch derived  
20 feedstock (1) is fed to a vacuum distillation column (2). In this column the feed (1) is separated into a vacuum gas oil fraction (3), a light base oil precursor fraction (4) and a heavy base oil precursor fraction (5). The viscosity of the targeted base oils will depend on the  
25 viscosity of the base oil precursor fractions (4,5). The desired viscosity of these precursor fractions may be obtained by manipulating the distillate cut point in step (a).

In Figure 1 the catalytic dewaxing step (b) is  
30 performed in two parallel operating catalytic dewaxing reactors (7,8). Alternatively one solvent or catalytic dewaxing reactor may also be used, wherein base oil precursor fractions (4,5) are processed alternatively (in

a so-called blocked out mode). The latter operation requires less reactors but on the other hand requires more intermediate storage and operational changes. Thus preferably two parallel-operated dewaxing reactors are used. In this manner dedicated dewaxing catalysts, in case catalytic dewaxing is used, may be advantageously used.

The effluents (9, 10) of the dewaxing step (b) as performed on fractions (4,5) are separated in one distillation column (14). In column (14) various base oil grades (16, 17, 13) may be obtained after topping off the lower boiling fraction (15). Applicants have found that it is now possible to simultaneously obtain at least a light base oil grade (16) having a kinematic viscosity at 100 °C of about 3.8 to 6 cSt which can be used in motor lubricant formulations, and a heavy base oil grade. In Figure 1 two heavy base oil grades are illustrated. Line-ups wherein only one heavy base oil grade is prepared are also possible. The heavy base oil grade (17) preferably has a kinematic viscosity at 100 °C of between 7 to 15 cSt. This base oil grade may be used as technical or medicinal white oil. A second heavy base oil grade (13) is also separated in column (14) having preferably a kinematic viscosity at 100 °C of above 15 cSt, more preferably above 17 cSt and even more preferably above 20 cSt. It may be advantageous to recycle part of the heavy grade (13) to the catalytic dewaxing reactor (8) in order to control the quality of said heavy base oil grade (13). In column (14) more grades (not shown) may be obtained having a kinematic viscosity at 100 °C of between 2 and 4 cSt. The top fraction (15) boiling below the base oil grades can be

used as fuel (gas oil, kerosene, naphtha, LPG) blending component.

In Figure 2 the effluent (10) is first separated in a heavy base oil column (11) into the heavy base oil (13) as described above and a lower boiling fraction (12). This lower boiling fraction (12) is preferably supplied to the base oil distillation column (14) as shown, fed to reactor (7) or to vacuum distillation column (2).

The viscosity of the heavy base oil grade (17) may be controlled by adjusting the cut point in distillation column (2). Alternatively the viscosity of base oil grade (17) may be adjusted by adding some of the heavy base oil fraction (6) to the light base oil precursor fraction (4) before performing step (b).

In this application reference is made to kinematic viscosity as measured by ASTM D 445 and to pour point as measured by ASTM D 97-93.

The invention will be illustrated with the below non-limiting examples.

#### Preparation of the dewaxing catalyst

MTW Type zeolite crystallites were prepared as described in "Verified synthesis of zeolitic materials" as published in Micropores and mesopores materials, volume 22 (1998), pages 644-645 using tetra ethyl ammonium bromide as the template. The Scanning Electron Microscope (SEM) visually observed particle size showed ZSM-12 particles of between 1 and 10  $\mu\text{m}$ . The average crystallite size as determined by XRD line broadening technique was 0.05  $\mu\text{m}$ . The crystallites thus obtained were extruded with a silica binder (10% by weight of zeolite, 90% by weight of silica binder). The extrudates were dried at 120 °C. A solution of  $(\text{NH}_4)_2\text{SiF}_6$  (45 ml of 0.019 N solution per gram of zeolite crystallites) was

5 poured onto the extrudates. The mixture was then heated at 100 °C under reflux for 17 h with gentle stirring above the extrudates. After filtration, the extrudates were washed twice with deionised water, dried for 2 hours at 120 °C and then calcined for 2 hours at 480 °C.

The thus obtained extrudates were impregnated with an aqueous solution of platinum tetramine hydroxide followed by drying (2 hours at 120 °C) and calcining (2 hours at 300 °C). The catalyst was activated by reduction of the platinum under a hydrogen rate of 100 l/hr at a temperature of 350 °C for 2 hours. The resulting catalyst comprised 0.35% by weight Pt supported on the dealuminated, silica-bound MTW zeolite.

#### Example 1

15 A partly isomerized Fischer-Tropsch derived wax having the properties as in Table 1 was distilled into a light base oil precursor fraction boiling substantially between 390 and 520 °C and a heavy base oil precursor fraction boiling above 520 °C.

Table 1

Density at 70 °C (kg/l)	0.7874
T10wt% (°C)	346
T50wt% (°C)	482
T90wt% (°C)	665
Wax congealing point (°C)	48

20 The heavy base oil precursor fraction was contacted with the above-described dewaxing catalyst. The dewaxing conditions were 40 bar hydrogen, WHSV = 1 kg/l.h, a temperature of 340 °C and a hydrogen gas rate of 700 Nl/kg feed.

The dewaxed oil was distilled into two base oil fractions having the properties listed in Table 2.

Table 2

	Light base oil	Heavy base oil
Boiling range of base oil product (°C)	390-520	>520
Yield on feed to dewaxer	6.2	54.3
Density at 20 °C (kg/l)	0.8144	0.8336
Pour point (°C)	Not measured	-42
Kinematic viscosity at 100 °C (cSt)	4.339	15.95
Viscosity Index	136	168
Average molecular weight	403	692

5 The light base oil precursor fraction was also catalytically dewaxed by contacting with the above described dewaxing catalyst. The dewaxing conditions were 40 bar hydrogen, WHSV = 1 kg/l.h, a temperature of 310 °C and a hydrogen gas rate of 700 Nl/kg feed.

The dewaxed oil was distilled into two base oil fractions having the properties listed in Table 3.



Table 3

Targeted oil grade	Base oil grade-4	Base oil grade-5.5
Targeted Boiling range of base oil product (°C)	400 - 455	420 - 520
Yield on feed to dewaxer	33.7%	63.3%
Density at 20 °C (kg/l)	0.8124	0.8183
Pour point (°C)	-32	-22
Kinematic viscosity at 100 °C (cSt)	4.00	5.537
Viscosity Index	132	144
Average molecular weight	385	451
T(10%), (50%), (90%) from TBP-GLC	397 / 430 / 456	417 / 462 / 522

Above, the distillation of the effluents of the dewaxing of the heavy and light base oil precursor fractions was done separately. It will be clear to the skilled person that the said effluents can also be combined before distillation into the various base oil products.

#### Example 2

Example 1 was repeated starting party isomerized Fischer-Tropsch derived wax having the properties as listed in Table 4. This feed was distilled into a light base oil precursor fraction boiling substantially between 390 and 520 °C and a heavy base oil precursor fraction boiling above 520 °C.

Table 4

T10wt% (°C)	549
T50wt% (°C)	656
T90wt% (°C)	> 750
Congealing Point (°C)	+106
Viscosity $\nu_k$ at 150°C	15.07 cSt

The heavy base oil precursor fraction was contacted with the above-described dewaxing catalyst. The dewaxing conditions were 40 bar hydrogen, WHSV = 1 kg/l.h, a temperature of 355°C and a hydrogen gas rate of 700 Nl/kg feed.

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The dewaxed oil was distilled into two base oil fractions having the properties listed in Table 5.

Table 5

	Light base oil	Heavy base oil
Boiling range of base oil product (°C)	390-520	>520
Yield on heavy feed to dewaxer	7.7	47
Density at 20 °C (kg/l)	0.8191	0.829
Pour point (°C)	Not measured	-15
Kinematic viscosity at 100 °C (cSt)	5.315	26.65
Viscosity Index	132	157
Average molecular weight	435	788

Example 3

5 This example illustrates the use of a heavy Fischer-Tropsch derived base oil grade as part of a 5W-30 lubricant composition according to the so-called SAE J300 classification without having to use a viscosity modifier. The properties of the Fischer-Tropsch derived base oils and the resulting lubricant are presented in Table 6.

Table 6

	Light base oil	Heavy base oil	5W-30 lubricant formulation	Specification for a 5W-30 lubricant according to SAE J-300
Light base oil	100%		68.8	
Additive Package (*)			10	
Pour point depressant			0.2	
Heavy base oil		100%	21	
Analysis				
MRV @ -35 °C, centi Poise			13,415 and 13,475	< 60,000
Yield stress @ -35 °C			no yield stress	no yield stress
Vdccc @ -30 C , Poise	18.74		64.11	66.00 max.
Kinematic viscosity at 100 °C (cSt)	4.979	24.53	9.517	9.3 to 12.5
Kinematic viscosity at 40 °C (cSt)	25.22			-
PourPoint (°C)	-54	+12	-51	-

(\*) the additive package was a standard package not containing a viscosity modifier additive.